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COMPARISON OF MATRIX CRACKING IN HIGH TEMPERATURE AND LOWER TEMPERATURE PMCs FROM CRYOGENIC EXPOSURE (PREPRINT)

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Nonmetallic Materials Division**

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Comparison of Matrix Cracking in High Temperature and Lower Temperature PMCs from Cryogenic Exposure

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The behavior of a high temperature carbon / polyimide composite, T650 / AFR-PE-4, in a cryogenic environment was studied. The results were compared to results from similar testing of a carbon / epoxy and a carbon / bismaleimide composite in order to begin to scale the difficulties involved with using high temperature polymer matrix composites (PMCs) in cryogen containers on launch vehicles. T650 / AFR-PE-4 developed transverse cracks in all plies after fewer cycles than a carbon / bismaleimide (IM7 / 5250-4) when each was cycled between -196 °C and their respective maximum service temperatures. A change to a cross-ply resulted in a substantial reduction in the tendency toward a complete crack network in past work on IM7 / 5250-4. However, the same change from a [0/45/-45/90]_S lay-up to a [0/90]_{2S} lay-up produced only a small delay of 50 cycles in the formation of transverse cracks in all plies of the T650 / AFR-PE-4 samples. On the other hand, the lay-up change corresponded to a large permeability reduction possibly due to less delamination in the [0/90]_{2S} samples or due to some of the transverse cracks remaining near the sample edges. Transverse strength and Mode I toughness of unidirectional laminates were also measured at room temperature (RT) and -196 °C to determine sources of the increased damage.

I. Introduction

Studies have shown that there would be considerable advantage to using PMCs as a lighter weight and possibly lower cost option for the structure in liquid hydrogen tanks for launch vehicles.¹⁻² However, since a laminated composite contains layers with widely differing coefficients of thermal expansion it has a natural tendency for large internal stresses to develop at low temperatures. Further, these residual stresses have the potential to propagate non-structural cracks during the thermal cycling that occurs when a multi-mission vehicle is fueled and flown multiple times.³⁻⁵ Much research has been directed toward an understanding of which combinations of fiber, matrix and ply lay-up are best for this type of application. Several achievements have been demonstrated in the tracking and containment of cracks that can lead to excessive permeability, the modeling of material and geometric parameters that affect permeability, and the design of composites with lower cure temperatures and lower residual stresses for cryogenic use. Further, Robinson¹ has shown that greater (than originally thought) tank wall permeation rates should be safe during the short duration of a launch to orbit since the area enclosed between the hydrogen and oxygen tanks where gases may accumulate is vented to the ambient environment that quickly becomes oxygen depleted. In this way, gathering sufficient hydrogen and oxygen together to cause a problem is difficult.

In view of these positive indicators researchers are now studying ways of pushing the envelope of composite-use in cryogenic environments further such as using high temperature PMCs – composites with a temperature capability significantly beyond the 120 °C to 177 °C upper range of carbon / epoxies. High temperature PMCs would have a major advantage in the cryogenic tank application. Using a PMC with a greater temperature capacity for the liquid hydrogen tank holds the promise of reducing the weight of thermal protection applied to the outside of the vehicle since the interior composite structure of the launch vehicle could be allowed to get hotter during and after atmospheric re-entry. On the other hand, the greater cure temperature of high temperature PMCs results in a composite with even greater residual stresses at cold temperatures than are induced in carbon / epoxies, and therefore the tendency for transverse cracking and delamination would increase.^{4,6} As a result, further assessment of high temperature PMCs under these severe conditions is needed.

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Relatively few studies have been completed to evaluate high temperature polymer matrix composites for use in a cryogenic environment.⁷⁻⁹ In one such effort by Bechel and Arnold,⁷ T650 / AFR-PE-4 and T650 / BIM-15 - both with service temperatures considerably greater than for carbon / epoxy or carbon / bismaleimide composites - were thermally cycled between -196 °C and 177 °C. Ply-by-ply crack densities and the through-thickness permeability were shown to be significantly greater than for a carbon / bismaleimide composite with a maximum service temperature closer to that of high performance carbon / epoxies. Also, they determined that when T650 / AFR-PE-4 was subjected to a harsher -196 °C and 315 °C cycle there was a only a moderate increase in damage and a small increase in permeability.⁷ In the current work, the effect of a lay-up change on the development of damage and permeability in the same T650 / AFR-PE-4 composite was investigated. Also, matrix-dominated unidirectional properties were measured to look for causes of the differences in cracking in T650 / AFR-PE-4 versus lower temperature carbon / polymer composites. To this end, the transverse strength and the Mode I toughness under ambient conditions and while submerged in liquid nitrogen were measured and compared with the same properties from IM7 / 5250-4 (carbon / bismaleimide) and IM7 / 977-2 (carbon / epoxy).

II. Experimental

A. Material

Thermal cycling from cryogenic to an elevated temperature, permeability testing, and mechanical property measurements were conducted on a carbon / polyimide composite with a maximum continuous dry service temperature that placed it in the category of high temperature PMCs. It consisted of intermediate modulus T650 carbon fibers from Cytec reinforcing a 315 °C maximum service temperature addition-polyimide matrix, AFR-PE-4, from Maverick. It was chosen because it is representative of high temperature, high performance structural polymer matrix composites used in the aerospace industry. The composite panels were hand laid-up and autoclave cured. 50 mm by 50 mm square [0/90]_{2S} samples with the 0° plies parallel to one edge were used for the cryogenic cycling and permeability testing. Samples for the mechanical testing were cut from an 8 ply unidirectional panel. The plies were 0.14 mm thick plies in each of the panels.

B. Cryogenic Cycling / Damage Measurement

A custom-made thermal cycler was used to move samples between a dewar of liquid nitrogen (LN₂), an ambient air fan, and an oven. Both the top of the LN₂ dewar and the bottom of the oven remained open during cycling. Based on measurements of temperature equilibration times on samples with an embedded thermocouple, a cycle of 2 minutes in the LN₂ followed by 5 minutes at RT and 5 minutes in the oven was used. Samples were polished on perpendicular edges prior to cycling, and cracks were counted on the sample edges using an optical microscope at 200X. Only transverse cracks that extended fully through the thickness of a ply were counted and the crack densities in symmetric plies were averaged from 4 samples.

C. Permeability Measurements

Permeability is defined here as the flow rate of helium through the sample. The permeability experiment is shown in Figure 1. A differential pressure was created across the sample to potentially create a flow of helium gas through the sample and into a 14 L control volume (CV). The gas flow rate was determined by measuring the increase in pressure in the CV as a function of time with a pressure transducer of 1×10^{-3} torr resolution. The rate of pressure change was then converted to a flow rate using the ideal gas law. The vacuum chamber on the left in Figure 1 is the CV, and the smaller vacuum chamber on the right provided vacuum for a mass spectrometer. During testing, a precision leak valve was used to transfer a small gas sample from the CV to the mass spectrometer to verify that the CV pressure increase was due at least partially to helium flowing through the sample.

The sample was sealed between two "sample chambers" each consisting of a vacuum flange and a Viton o-ring with a 3.05 cm ID. The upstream chamber contained helium at 0.28 MPa (40 psi), and the downstream chamber was connected to the vacuum of the CV. After cycling, cracks in the surface plies of the samples provided a path for ambient air to bypass the seal on the downstream side of the sample and to flow into the sample chamber and CV. This "background flow" was measured for each sample after each increment of cycling prior to permeability testing by monitoring the CV pressure with vacuum applied to both sides of the sample. In this way, the background flow was separated from helium flow through the sample. Through-thickness helium flows could not be accurately separated from the background flow of air until the helium flow reached approximately 1.1×10^{-7} scc / s-cm². Permeability was measured at RT, and the test length was 400 seconds or less depending on how the helium flow rate through the sample compared to the background flow.

D. Mechanical Property Measurements

Compact tension toughness testing of the T650 / AFR-PE-4 unidirectional composite was conducted according to ASTM E399. The specimens were 20 mm x 20 mm square and 1.14 mm thick. A saw-cut pre-crack was added to each sample and extended to form a natural crack by putting a C-clamp across the specimen and lightly tapping a razor blade into the saw cut. The resulting cracks (combined saw cut and natural crack extension), were typically 4.5 mm long. The fiber direction for the specimens was parallel to the crack growth direction. The specimens were pin-loaded in a servo-hydraulic load frame at 0.00076 cm/sec until failure occurred. The RT specimens were tested in the ambient laboratory environment. The specimens tested at -196°C were submerged in LN₂ in a custom stainless steel container and fixture that fit between the load-frame grips. The specimens were allowed to equilibrate at each temperature for at least 10 minutes before testing. Similarly, transverse tension testing was conducted on the unidirectional AFR-PE-4 composite at RT and at -196 °C according to ASTM D3039.

III. Results

A. Transverse Crack Densities

T650 / AFR-PE-4 cross ply samples were thermally cycled between the -196 °C temperature of liquid nitrogen and the 315 °C maximum service temperature of AFR-PE-4. The damage accumulation is compared here with the results for the same material with a quasi-isotropic lay-up and another lower temperature material with the same two lay-ups. As has been shown in past work, the [0/45/-45/90]_S lay-up is commonly more susceptible than the [0/90]_{2S} lay-up to the formation of a complete network of transverse cracks and delaminations that can result in significant permeability given that the ply thickness and the thermal cycle profile are the same.³ In Figure 2 the crack densities for each ply of the T650 / AFR-PE-4 [0/45/-45/90]_S samples are shown as a function of the number of -196 °C to 315 °C thermal cycles.⁷ Figure 3 has the crack densities for the [0/90]_{2S} samples, and similar data from past work for samples of IM7 / 5250-4 of the same lay-ups³ is plotted in Figures 4 and 5. The ply thickness was constant at 0.14 mm for the materials represented in each of the four figures. However, the thermal cycle was not constant since it consisted of a -196 °C to 177 °C cycle for IM7 / 5250-4 and a -196 °C to 315 °C cycle for T650 / AFR-PE-4. Each of the materials was cycled between LN₂ and an upper temperature that is near the max continuous service temperature for that material. This comparison between data for different thermal cycle profiles is done because a composite with an AFR-PE-4 matrix is unlikely to be chosen for a cryogenic tank application unless it is to be used in a more severe environment (higher temperature) that takes advantage of its high-temperature capability. The reasons for this include more involved processing for AFR-PE-4, a greater cost, and reduced mechanical properties (some – not all) at RT and below.

There are multiple differences in the damage trends among the four figures. First, in both materials, for a given number of cycles, the transverse crack density of the surface plies is greater in the [0/90]_{2S} samples than in the [0/45/-45/90]_S samples, but the onset of cracking is delayed and / or the crack density is initially reduced in the other plies. However, this trend is much more pronounced in the IM7 / 5250-4 data. The change of lay-up in the lower temperature carbon / bismaleimide to a cross-ply was very effective in keeping one or more plies un-cracked. On the other hand, in T650 / AFR-PE-4 the change to a cross-ply delayed the cracking of all plies by only an additional 50 cycles.

The crack density in the plies with the lowest crack density – referred to as the “minimum crack density” – was also significantly altered. The minimum crack density quickly reached 3.5 cracks / cm in the AFR-PE-4 [0/90]_{2S} samples which approached the minimum crack density of 4.5 cracks / cm in the [0/45/-45/90]_S samples by 250 cycles. This rapid trend is surprising in lieu of the work by Bechel, et al.³ in which they demonstrated a 15 times reduction in minimum crack density in IM7 / 5250-4 after 1250 cycles of -196 °C to 177 °C when a [0/90]_{2S} lay-up was used versus a [0/45/-45/90]_S lay-up, and the minimum crack density remained at only 0.44 cracks/cm for the [0/90]_{2S} lay-up *after 1250 cycles*. I.e., the positive effect of using a cross-ply lay-up lasted for up to 1000 cycles longer in the lower temperature carbon / bismaleimide than in the higher temperature carbon / polyimide. Consequently, lay-up changes, in general, would not be expected to be nearly as effective as a method of controlling damage leading to permeability in higher temperature PMCs as in some of the lower temperature PMCs.

B. Permeability Versus Thermal Cycles

The permeability of the T650 / AFR-PE-4 samples was measured after 0, 15, 30, 75, 125, 175, and 250 thermal cycles in the current work for a [0/90]_{2S} lay-up and in past work⁷ for a [0/45/-45/90]_S lay-up for the same -196 °C

and 315 °C thermal cycle. The permeability measured at RT after 250 cycles was, on average, approximately 9×10^{-5} scc / s-cm² for the [0/45/-45/90]_{2S} samples. But for the samples from the [0/90]_{2S} lay-up for each of the increments of cycles up through 250 cycles the permeability was less than 1.1×10^{-7} scc / s-cm² (the resolution of the test). However, qualitatively it was determined that there was *some* helium flow through the [0/90]_{2S} samples after 250 cycles (but not after fewer cycles) since there was a noticeable increase in helium partial pressure on gas samples analyzed with the mass spectrometer after each permeability test on the samples cycled 250 times. Unfortunately, with the large background flow it was not possible to quantitatively determine the helium flow on these same samples. According to Figures 2 and 3, the crack densities on the edges of the T650 / AFR-PE-4 samples for both lay-ups were nearly equal in severity after 250 cycles in terms of the ability of the minimum crack density in plies 3 and 6 to limit gas flow through the samples. I.e., their tendency to allow leakage through the sample should have been similar if the damage on the edge was a reliable indicator. Clearly this was not the case since there was a very large effect on the permeability from a change in lay-up.

The large difference in permeability may be a consequence of several factors such as the very likely lack of stitch cracks (short cracks that propagate from a crack in a neighboring ply) in the [0/90]_{2S} lay-up³ or a difference in the amount of delamination (not measured here) that is essential to link the transverse cracks in adjacent plies. Another possibility is that the cracks did not propagate far from the edge of the sample in some of the plies¹¹⁻¹² such as the non-surface plies and thinner plies number 2, 3, 6, and 7. In the quasi-isotropic lay-up this would not stop formation of a complete crack network because short stitch cracks form relatively easily and are not cracks that initiate on the edges. On the other hand, in the cross-ply, stitch cracks normally do not form so it can be more difficult to complete the network. At any rate, even though the crack densities were relatively high (as seen on the edges) in both lay-ups of T650 / AFR-PE-4, the effect of choosing a lay-up that doesn't allow stitch cracking had a large effect on permeability.

C. Transverse Strength and Toughness

Two of the basic unidirectional composite properties – transverse strength and Mode I fracture toughness – were measured since they are likely to relate closely to the capability of a composite to resist transverse cracking. Figure 6 shows a comparison of the transverse strength of T650 / AFR-PE-4 with IM7 / 5250-4 and IM7 / 977-2. The comparison is made with IM7/5250-4 (max service temp 204 °C) and IM7/977-2 (max service 120 °C) since both are commonly used in aerospace structures within their respective service temperature regimes. I.e., they have a mix of mechanical property and processing characteristics that may also make them good candidates for cryogenic tanks for launch vehicles. In addition, IM7 / 977-2 has been used in multiple studies of the cryogenic performance of composites and in subscale component test articles because of its excellent resistance to matrix cracking at cryogenic temperatures compared to many other carbon fiber composites with toughened epoxy matrices. As Figure 6 indicates the transverse strength of T650 / AFR-PE-4 was very similar to that of IM7 / 977-2 at RT and only 7% lower at -196 °C. The largest difference was a 22% lower transverse strength for T650 AFR-PE-4 compared at -196 °C to that of IM7 / 5250-4. Note, the 73 MPa transverse strength measured here for T650 / AFR-PE-4 at RT is similar to the transverse strength measured by Whitley and Collins.⁸ However, the nearly constant transverse strength at -196 °C versus at RT is much different than Whitley and Gates⁹ measured for another high temperature carbon / polymer composite, IM7 / PETI5 (glass transition temperature 267 °C), which had a transverse strength of 46.7 MPa at RT but a reduced transverse strength of 21.0 MPa at -196 °C.

In Figure 7 the Mode I fracture toughness of the unidirectional T650 / AFR-PE-4 is compared to the toughness of the two lower temperature composites used for comparison of the transverse strength measurements. The toughness is much lower than for either IM7 / 5250-4 or IM7 / 977-2. The measured value of 1.0 MPa-m^{1/2} at RT for T650 / AFR-PE-4 is only 55% of the value of 1.8 MPa-m^{1/2} for IM7 / 977-2 and only 45% of the IM7/977-2 value at -196 °C. However, the trend for variation in toughness of T650 / AFR-PE-4 versus temperature is similar to the trend seen in the other two materials and in other carbon / toughened epoxies as shown by Donaldson, et al¹⁰ (for example for IM7 / 977-3) in that the toughness at -196 °C is equal to or slightly greater than its value at RT. Despite the adequate transverse strength, the use of T650 / AFR-PE-4 in cryo-cyclic environments clearly has a major barrier to be overcome with the reduced toughness.

IV. Conclusions

T650 / AFR-PE-4 was evaluated for cryogenic use by measuring mechanical properties, resistance to cracking caused by cycling, and helium gas permeability. The transverse strength of AFR-PE-4 was shown to be comparable at both RT and -196 °C to the transverse strength measured at the same temperatures for IM7 / 5250-4 and IM7 /

977-2. The largest difference was a 20% decrease at -196 °C versus IM7 / 5250-4. The toughness of T650 / AFR-PE-4, on the other hand, was 45-55% lower when compared to the toughness of these other materials. Notably, the toughness for AFR-PE-4 was slightly larger at -196 °C than at RT (1.1 MPa-m^{1/2} vs. 1.0 MPa-m^{1/2}). In addition, the use of a [0/90]_{2S} instead of a [0/45/-45/90]_S lay-up was not nearly as effective at reducing damage in the higher temperature T650 / AFR-PE-4 as in the lower temperature IM7 / 5250-4 when both were cycled between -196 °C and their respective maximum service temperatures. The number of cycles at which all plies cracked and the minimum crack density were monitored as indicators of the tendency for permeability. The [0/90]_{2S} samples of AFR-PE-4 had the last remaining un-cracked plies begin to crack only 50 cycles later than was observed in the [0/45/-45/90]_S samples. In addition, the minimum crack density increased quickly to 75% of the value measured for [0/45/-45/90]_S samples after only another 50 cycles (250 total). Finally, permeability for T650 / AFR-PE-4 was measured at RT after several intervals of the -196 °C to 315 °C cycles. Despite the similarities in the minimum crack density and overall crack density for the [0/90]_{2S} and the [0/45/-45/90]_S samples, the permeability of the [0/90]_{2S} samples was at least 2 orders of magnitude lower.

The lower permeability of the cross-ply samples of T650 / AFR-PE-4 leaves room for optimism. However, it is clear from the damage comparisons between laminates and between the T650 / AFR-PE-4 and IM7 / 5250-4 samples that the use of higher temperature PMCs in cryogenic environments will be a challenge. The more severe operating environment, the limited choice of materials, and the fact that it may be necessary to work with a PMC with a significantly lower toughness at cryogenic temperatures all work against the higher temperature PMCs. As a result, it will likely be necessary to move beyond lay-up changes and intelligent material down-selection as methods for adequately controlling permeability in this class of materials for the reusable cryogenic tank application.

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Figure 1: Permeability measurement apparatus

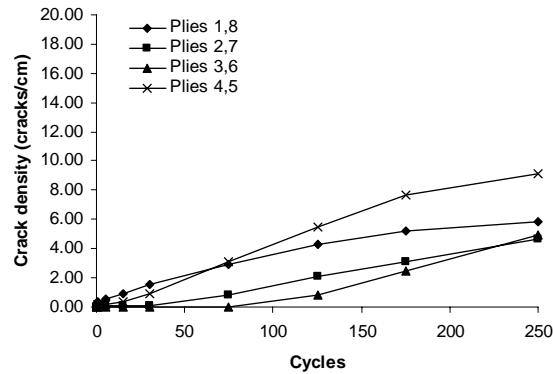


Figure 2: Damage in T650/AFR-PE-4 [0/45/-45/90]_s (-196 °C to 315 °C thermal cycling)⁷

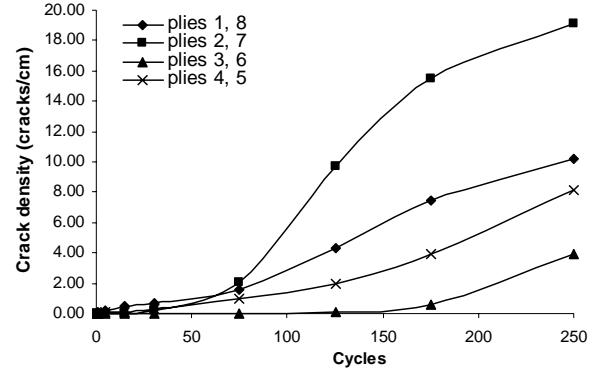


Figure 3: Damage in T650/AFR-PE-4 [0//90]_{2s} (-196 °C to 315 °C thermal cycling)

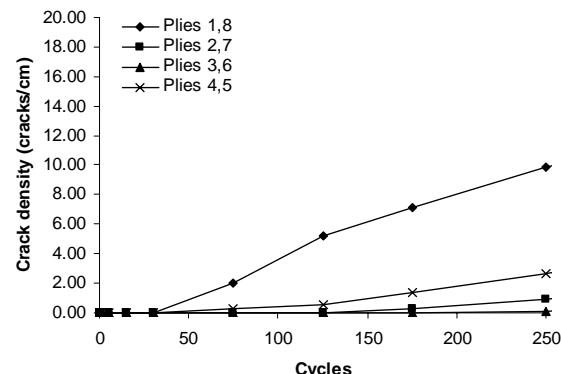


Figure 4: Damage in IM7/5250-4 [0/45/-45/90]_s (-196 °C to 177 °C thermal cycling)

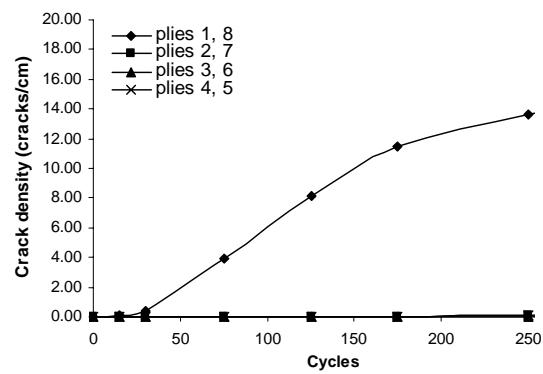


Figure 5: Damage in IM7/5250-4 [0/90]_{2s} (-196 °C to 177 °C thermal cycling)

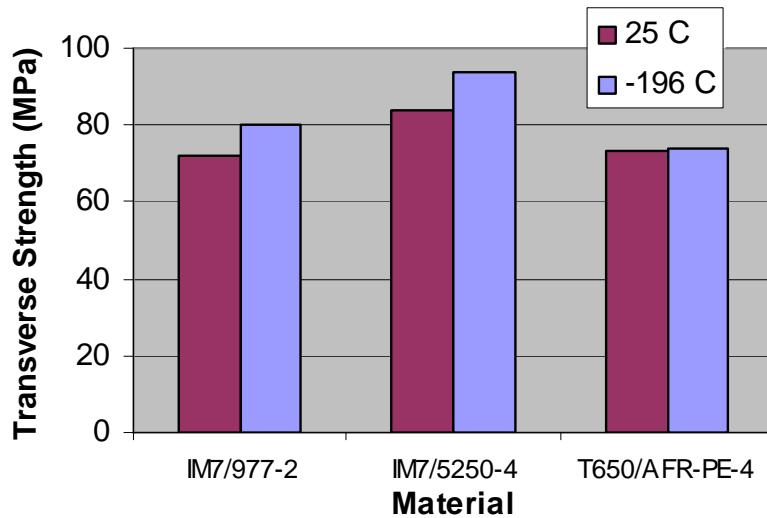


Figure 6: Transverse strength of T650/AFR-PE-4 compared to previous measurements for IM7/977-2 and IM7/5250-4

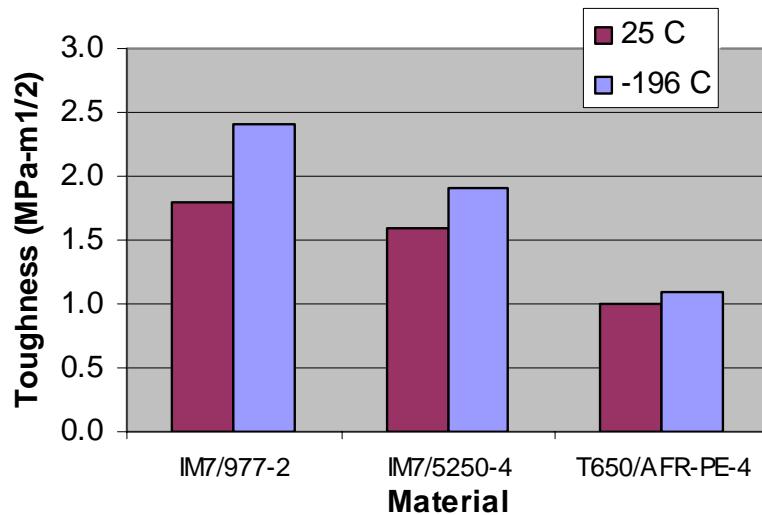


Figure 7: Mode I toughness of T650/AFR-PE-4 compared to previous measurements¹⁰ for IM7/977-2 and IM7/5250-4